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PART I

KINETICS AND MECHANISMS OF THERMAL DEGRADATION OF POLYMERS USING
TIME-OF-FLIGHT MASS SPECTROMETRY FOR CONTINUOUS GAS ANALYSIS

H. L. Friedman and G. A. Griffith

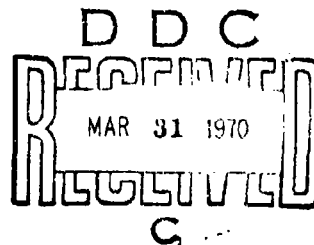
General Electric Company

TECHNICAL REPORT AFML-TR-69-343, PART I

March 1970

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TIME-OF-FLIGHT MASS SPECTROMETRY FOR CONTINUOUS GAS ANALYSIS**

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FOREWORD

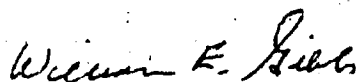
This report was prepared by the General Electric Company under USAF Contract No. F-33615-69-C-1318. The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules," and was followed by USAF Contracts No. F-33615-67-C-1372 and F-33615-68-C-1107. It was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. Ivan J. Goldfarb, MANP, Project Engineer.

This work was performed in the Space Sciences Laboratory of the Valley Forge Space Technology Center, King of Prussia, Pennsylvania. The following personnel participated in this program: Dr. H. L. Friedman, Principal Investigator and Mr. G. A. Griffith, Technician.

The authors gratefully acknowledge the help given to them by several others, including Dr. H. W. Goldstein, Dr. G. Liebling, Mr. J. R. Kruse, and Mr. L. J. Napaluch, Jr. Discussions with and advice from Dr. I. J. Goldfarb was also very helpful.

This report covers work from January 1969 to October 1969. The report was submitted by the author in December 1969.

This technical report has been reviewed and is approved.



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ABSTRACT

Research was continued using mass spectrometric thermal analysis (MTA) to study the thermal degradation of various polymers. Several samples of bis benzimidazo benzophenathroline (BBB) polymer and its ladder (BBL) polymers were successfully subjected to MTA. Quantitative results were obtained for ordinary and end-capped BBL polymers, and the effects of end-capping were discussed. BBB runs were carried out in modified fashions that allowed greater frequency of scanning of a limited mass range. The effects of varying the frequency were discussed. The results for BBL polymers and for the present and earlier BBB polymers were compared. A discussion on some aspects of the mechanism of thermal degradation of aliphatic polyesters was included, as the result of reviewing earlier data.

Calibration results were reported for seventeen compounds. Pumping coefficients for thirty three compounds were compared.

Tests were carried out for new furnace systems in a more modern time-of-flight mass spectrometer, which was equipped with a differentially pumped region near the electron beam.

Computer programs are in the process of being rewritten for a new computer and to permit greater flexibility in experimental technique and in data processing.

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
I	INTRODUCTION	1
II	MODIFICATION OF MTA APPARATUS	2
III	COMPUTER PROGRAM CHANGES	6
IV	CALIBRATION OF PURE COMPOUNDS	7
	A. Sensitivity and Fragmentation Patterns	7
	B. Pumping Coefficients of Pure Compounds	7
V	MTA OF POLYMERS	18
	A. Bis Benzimidazo Benzophenathroline Ladder Polymers	18
	B. Bis Benzimidazo Benzophenathroline Polymers	22
VI	DISCUSSION	28
	A. Bis Benzimidazo Benzophenathroline Polymers and Ladder Polymers	28
	B. Aliphatic Polyesters	30
VII	CONCLUSIONS	31
VIII	RECOMMENDATIONS FOR FUTURE WORK	32
	REFERENCES	33

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Pyrolysis Platform with Thermocouple and Sample Pan in Place	4
2	Flange and Furnace Assembly	5
3	Pumping Coefficients for Various Molecules	17
4	Representative Standardized MTA Results for Bis Benzimidazo Benzophenathroline Ladder Polymer (BBL-SN2)	20
5	Representative Standardized MTA Results for End-Capped Bis Benzimidazo Benzophenathroline Ladder Polymer (BBL-SN2-EC)	21
6	MTA Plot at m/e-28 for Single Peak Run on Celanese Bis Benzimidazo Benzophenathroline Polymer	25
7	MTA Plot at m/e-28 for 40 Peaks/Scan Run on Celanese Bis Benzimidazo Benzophenathroline Polymer	27
8	Standardized MTA Plot at m/e-28 for Earlier Bis Benzimidazo Benzophenathroline Polymer (aa-BB-2)	29

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	MASS SPECTRA OF CALIBRATION COMPOUNDS	8 - 15
II	PUMPING COEFFICIENTS FOR VARIOUS MOLECULES	16
III	SUCCESSFUL MTA EXPERIMENTS	19
IV	MTA RESULTS FROM BIS BENZIMIDAZO BENZO- PHENATHROLINE LADDER POLYMER (BBL-SN2)	23
V	MTA RESULTS FROM END-CAPPED BIS BENZIMIDAZO BENZOPHENATHROLINE LADDER POLYMER (BBL-SN2- EC)	24

SECTION I

INTRODUCTION

During the past few years, through a continuing research program of the Air Force Materials Laboratory and its contractors, many new classes of thermally stable polymers have been and are being synthesized. The thermal stability of most of these classes of materials has been investigated by thermogravimetry. This method has led to some qualitative relationships between chemical structure and behavior in the thermobalance. Quantitative relationships between these properties are not available.

The previous work related to the present program is described in five reports (refs. 1-5). The first stage attempted quantitative measurements through vacuum microthermogravimetry (refs. 1,2). This was later supplanted by mass spectrometric thermal analysis (MTA) (refs. 1-5). Automatic data collecting and processing instrumentation and methods were then developed to handle the large quantity of data generated in a single MTA experiment (refs. 2-4). A considerable effort was related to assuring reasonable accuracy in the data collected by automatic methods (refs 3-5). The type of polymers studied in the earlier stages have included polybenzimidazoles (refs. 1-3,5), aliphatic polyesters (refs. 4,5), aliphatic-aromatic polyesters (ref. 5), aromatic polyesters (ref. 5), aliphatic polyamides (ref. 4), aliphatic-aromatic polyamides (ref. 5), aromatic polyamides (refs. 4,5), and bis benzimidazo benzophenathroline polymer (refs. 4,5). Five papers by Space Science Laboratory authors (refs. 6-10) and three papers by Air Force Materials Laboratory authors (refs. 11-13) are based on the earlier studies.

The first research (refs. 1-3) emphasized the relationship between structure and thermal stability of new high temperature polymers, and also emphasized the development of MTA. The more recent parts (ref. 4,5) stress the systematic application of MTA to explore the kinetics and mechanisms of thermal degradation of polymers in depth.

A brief review of the experimental method is appropriate at this point. Polymer samples weighing approximately 1 mg. are pyrolyzed in vacuum from room temperature to 1000°C at a rate of 10°C/min. The effluent gases are pumped into a time-of-flight mass spectrometer where 200 different pre-selected ionic masses are scanned repetitively every 108 seconds. Sample temperature, mass number, and ion intensity are recorded on perforated tape for each step in the mass scan. The data are then subjected to various data processing methods.

SECTION II

MODIFICATION OF MTA APPARATUS

The apparatus and method of operation were generally the same as described previously (refs. 4, 5). One of the components of the system has been somewhat troublesome, namely the scanner that switches the three parameters recorded on perforated tape. Mechanical and contact problems have arisen in the relay logic, which sometimes caused two identical gate voltage signals to be recorded consecutively. This alters the proper data acquisition sequence and influences later data processing. In order to maintain the proper sequence it was necessary to (1) clean the contacts very frequently, (2) adjust the relay springs very carefully, and (3) operate the system more slowly. The last factor continually reduced the number of points recorded per run. The old scanner has recently been replaced with a Digitec Model 634 unit, one that incorporates solid state logic.

A more modern mass spectrometer is available in the Space Sciences Laboratory, that offers some potential advantages. This instrument, which was described in reference 9, is equipped with a Knudsen Cell inlet cross and isolation valve. Thus a sample may be pyrolyzed in a differentially pumped zone near the electron beam of the mass spectrometer. Samples may be loaded and removed quite rapidly. In addition, use of a gettering pump allows the mass spectrometer to be maintained at high vacuum at all times. These features would allow for more efficient operation, reduced time delays due to the pumping delays and adsorption that occur in the present system, and greater ability to observe transitory products. The last two items could contribute to improved data for kinetic analysis. Another feature is that all permanent magnets are mounted on the exterior of the instrument. The aging of such magnets is thought to contribute to the gradual shifts that have been observed in mass discrimination (ref. 5). The possibility of changing the permanent magnets to electromagnets was investigated. It was found, however, that commercially available magnet systems are too sophisticated, and it would be more practical to fabricate electromagnets in the laboratory for this purpose.

A crude furnace was fabricated for the differentially pumped region of the newer mass spectrometer, but it was found that the ceramic furnace core outgassed excessively during programmed heating, and that the present programmer could not function properly with it. A special furnace was purchased to solve these problems. It was fabricated from a very dense ceramic material, and was designed to take a quantity of nichrome wire that was compatible with the programmer. A flange was fabricated to hold the furnace in place and to permit electric power to be brought to the furnace, and to provide electrical contact with the thermocouple for temperature measurement and control. A photograph of the thermocouple and sample pan in place in a quartz core,

is shown in Figure 1. The entire furnace assembly is shown in Figure 2. Programming tests showed adequate control, with a little less smoothness than the more massive external furnace. The nichrome windings burned out quite rapidly in tests, probably because of poor heat transfer in vacuum. Also, more outgassing was observed than would be considered desirable. An entirely different type of furnace would be required for this purpose.

J. R. Kruse and L. J. Napaluch have developed the concept of a peak finder to replace the present programmed mass selector. This system would utilize the present analog-to-digital conversion system, but would add several benefits including: (1) improved mass resolution; (2) recording data only when peaks are present; (3) improved accuracy; (4) obtaining data for each mass peak at shorter intervals, thus defining the peak more accurately; and (5) eliminate the need for assuring coincidence between the mass spectral peaks and programmed gate positions. It would be necessary to include a time signal generator, for there would be unequal time intervals between peak locations. Computer programs would have to be rewritten to process the new data format. The proposed system is based on missile observation technology, but requires some additional equipment and development. Its addition will be considered at a later stage of the program.

Several runs have been carried out where the data processing system has been used to record data for a single mass peak, or for just a few mass peaks at a much greater frequency than before. Because of greater time resolution, and the inherent statistical data fluctuations, these data have been found to be much more useful for kinetic analysis. Future plans are to carry out the usual 200 peak experiment first, and complete the usual data processing. Then examine the data and select the peaks that contain only the most important data. Then run a second experiment in which only these mass peaks are scanned, but with much greater frequency at each individual peak. This could only be accomplished at adjacent mass peaks with the current system. A flexible potentiometer has been designed to permit selection of up to 20 non-consecutive masses, and parts have been ordered.

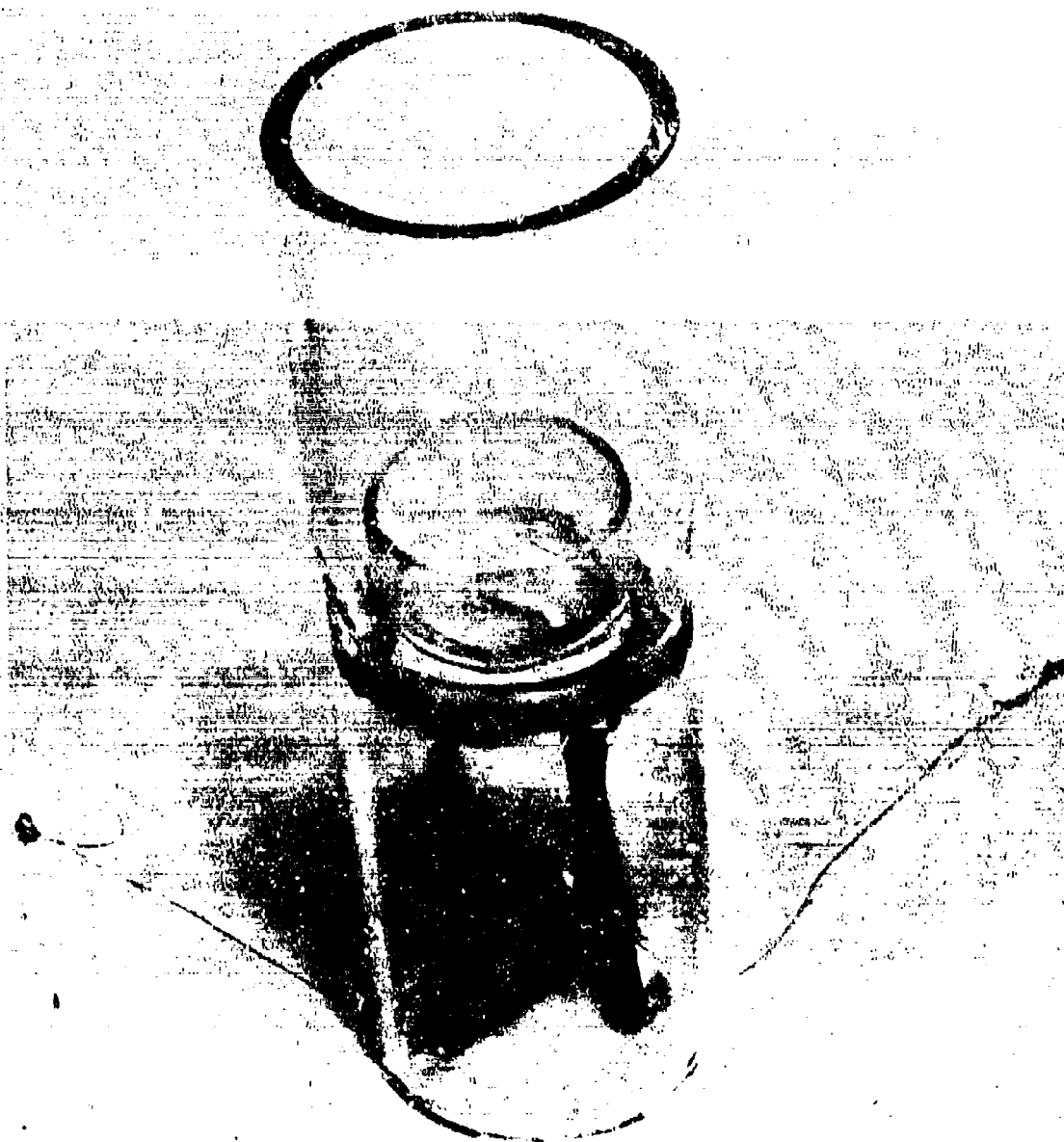


Figure 1. Pyrolysis Platform with Thermocouple and Sample Pan in Place

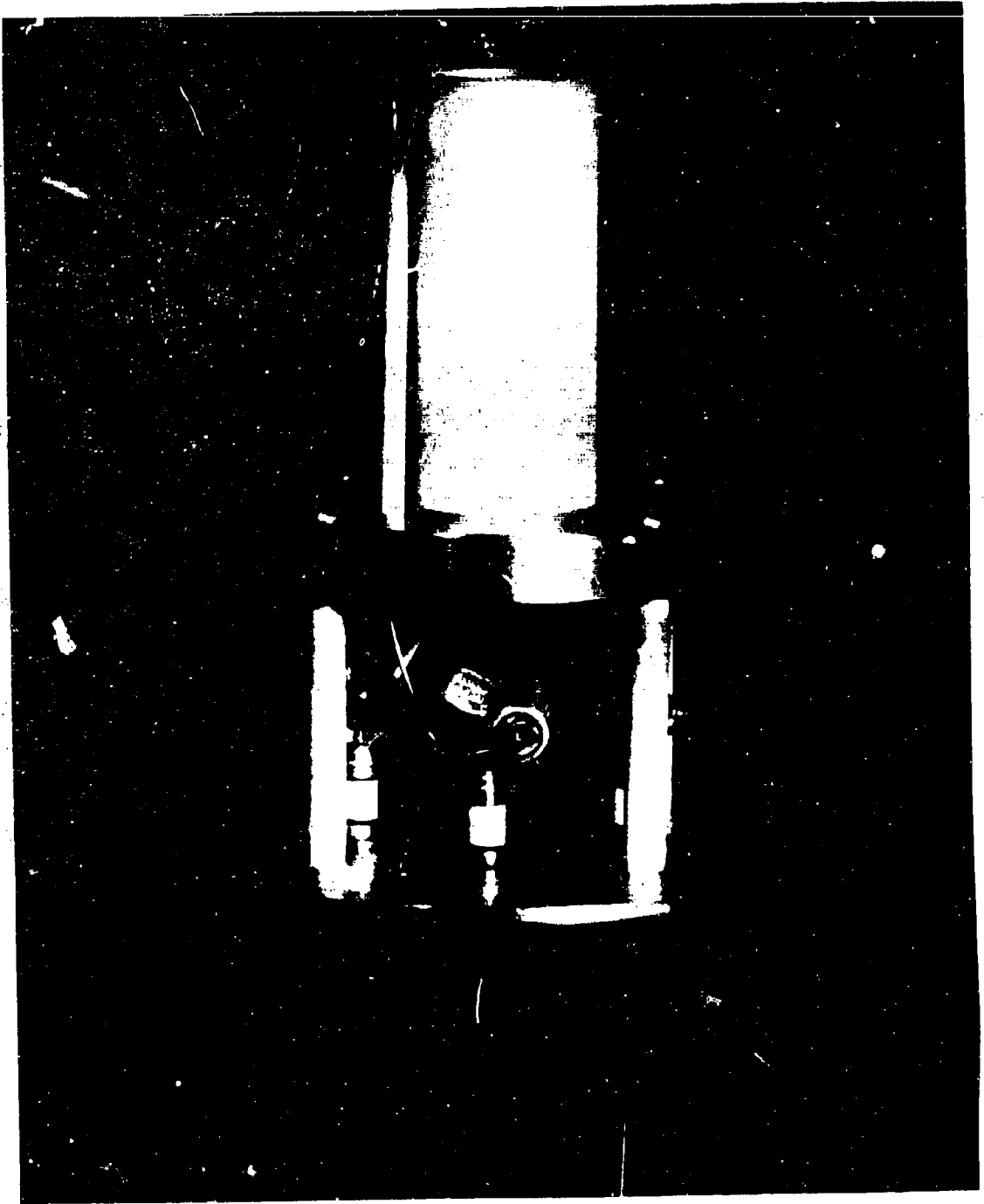


Figure 2. Flange and Furnace Assembly

SECTION III

COMPUTER PROGRAM CHANGES

Several kinds of computer program changes have been necessary during the period of this report. One type of change was caused by changing the computer at these facilities. The others were required for greater versatility. The computer programs were originally designed to handle three data words (temperature, gate voltage, and ion intensity) per point, 200 points per scan, and up to 70 scans per run. It is now desired to reduce the number of points per scan and to increase the number of scans per run.

Three main computer programs are utilized. The first is optical conversion of the perforated paper tape to a digital magnetic tape with the SDS Model 910 computer. This program has now been modified. The second program sorts the data from the magnetic tape, in sets, one for each mass number. That program has been written for the new computer (General Electric Model 635) and is being checked out. The third program prepares the graph plotting tape from the sorted tape. That program is also being written for the new computer, but is in an earlier stage of development. Because of insufficient resolution capabilities of the automatic graph plotter, one graph per sheet will be plotted, rather than nine, for those runs when 20 or fewer masses are scanned.

SECTION IV

CALIBRATION OF PURE COMPOUNDS

A. Sensitivity and Fragmentation Patterns

Calibration data have been obtained for seventeen compounds in addition to the thirteen listed in reference 5. The results are listed in Table I.

B. Pumping Coefficients of Pure Compounds

Thirty three compounds have now been subjected to calibration experiments; the thirty mentioned above, plus n-butane, hexachloroethane and hydrogen, the daily calibration standards. It seemed appropriate to investigate their pumping rates through the mass spectrometer leak. The slope, β , of the plots of log intensity vs. time, from which sensitivities were computed is given from theory as

$$\beta = \frac{2.303A}{V} \left(\frac{kT}{2\pi m} \right)^{1/2}$$

where A = leak area in cm.^2 , V = calibration volume in cm.^3 , k (Boltzman Constant) = 1.380×10^{-16} erg/ $^{\circ}\text{K}$ molecule, T = temperature in $^{\circ}\text{K}$, and m = mass in gm./molecule. Since all factors are constant, except for molecular weight, in the ideal case, a plot of β vs. reciprocal square root molecular weight should yield a straight line. The real values are listed in Table II and are plotted in Figure 3. A straight line is arbitrarily drawn from the origin through the value for hydrogen. Note that there is a considerable amount of scatter, and that values lie both above and below this line. The scatter probably reflects holdup due to adsorption and flow properties of the various molecules in the system. Values of $\beta(\text{M.W.})^{1/2}$ were determined for all thirty three compounds, and were found to average 0.0184, with the average deviation ± 0.0031 ($\pm 17\%$). The largest deviation was for hexachloroethane, -41% . There was some trend, where the lighter molecules gave higher values and the heavier molecules gave lower ones. Eleven molecules showed values appreciably greater than the average deviation, namely ethylene ($+37\%$), oxygen ($+29\%$), hydrogen sulfide ($+26\%$), methane ($+22\%$), carbon monoxide ($+22\%$), benzene (-27%), ammonia (-28%), acetic acid (-33%), furfuryl alcohol (-35%), benzonitrile (-37%) and hexachloroethane (-41%).

TABLE I
MASS SPECTRA OF CALIBRATION COMPOUNDS

AMMONIA, Sensitivity Coefficient = 0.419^a

$(I_{m/e}/I_{17})$		$(I_{m/e}/I_{17})$		$(I_{m/e}/I_{17})$	
<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>
15	4.4	17	100.0	18	2.9
16	79.3				

ACETYLENE, Sensitivity Coefficient = 0.841^a

$(I_{m/e}/I_{26})$		$(I_{m/e}/I_{26})$		$(I_{m/e}/I_{26})$	
<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>
12	0.4	24	5.9	26	100.0
13	4.3	25	20.7	27	2.6

METHANOL, Sensitivity Coefficient = 0.323^a

$(I_{m/e}/I_{31})$		$(I_{m/e}/I_{31})$		$(I_{m/e}/I_{31})$	
<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>
1	1.7	17	1.0	30	8.3
12	1.2	18	2.5	31	100.0
13	2.6	27	1.4	32	71.3
14	5.7	28	8.0	33	1.2
15	31.2	29	64.3		

PROPYLENE, Sensitivity Coefficient = 0.603^a

$(I_{m/e}/I_{41})$		$(I_{m/e}/I_{41})$		$(I_{m/e}/I_{41})$	
<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>
13	1.6	27	50.7	39	61.0
14	4.2	28	43.3	40	24.7
15	3.6	36	1.9	41	100.0
24	1.1	37	10.9	42	70.5
25	4.9	38	17.5	43	3.0
26	29.8				

^a Sensitivity ratio of peak with intensity ratio 100 to sensitivity of n-butane at m/e-43.

TABLE I (Continued)

MASS SPECTRA OF CALIBRATION COMPOUNDS

PROPANE, Sensitivity Coefficient = 0.570^a

$(I_{m/e}/I_{29})$		$(I_{m/e}/I_{29})$		$(I_{m/e}/I_{29})$	
<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>
14	2.0	30	2.4	41	17.4
15	6.4	36	0.6	42	11.5
26	10.6	37	4.2	43	37.5
27	45.3	38	7.3	44	56.9
28	68.7	39	24.3	45	1.6
29	100.0	40	3.5		

ACRYLONITRILE, Sensitivity Coefficient = 0.577^a

$(I_{m/e}/I_{53})$		$(I_{m/e}/I_{53})$		$(I_{m/e}/I_{53})$	
<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>
12	1.6	27	14.6	50	7.5
13	1.1	36	1.9	51	26.8
14	2.1	37	3.7	52	61.2
24	2.5	38	5.7	53	100.0
25	6.8	39	1.7	54	5.0
26	70.6				

ACETONE, Sensitivity Coefficient = 0.923^a

$(I_{m/e}/I_{43})$		$(I_{m/e}/I_{43})$		$(I_{m/e}/I_{43})$	
<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>
13	1.2	28	b	41	2.4
14	4.4	29	3.3	42	7.7
15	23.0	37	1.9	43	100.0
25	1.1	38	2.7	44	2.6
26	4.8	39	3.7	57	0.9
27	7.4	40	1.3	58	28.9

^a Sensitivity ratio of peak with intensity ratio of 100 to sensitivity of n-butane at m/e-43.

^b Difficult to evaluate because of air background. Literature indicates value of approximately 3.0.

TABLE I (Continued)

MASS SPECTRA OF CALIBRATION COMPOUNDS

ISOPROPANOL, Sensitivity Coefficient = 0.992^a

$(I_{m/e}/I_{45})$		$(I_{m/e}/I_{45})$		$(I_{m/e}/I_{45})$	
<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>
14	2.0	37	1.2	43	18.7
15	7.7	38	1.7	44	5.9
26	1.4	39	4.5	45	100.0
27	13.7	40	1.2	46	2.9
29	6.4	41	4.9	59	3.8
31	5.0	42	3.7		

ACETIC ACID, Sensitivity Coefficient = 0.836^a

$(I_{m/e}/I_{43})$		$(I_{m/e}/I_{43})$		$(I_{m/e}/I_{43})$	
<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>	<u>m/e</u>	<u>x100</u>
12	2.3	29	17.6	44	6.0
13	5.4	30	1.0	45	89.8
14	12.3	31	4.5	46	1.9
15	40.0	37	1.4	47	1.1
16	6.4	38	3.0	51	3.8
17	8.0	41	7.2	52	1.6
18	23.3	42	17.4	57	1.5
25	1.2	43	100.0	60	48.7
27	7.2				

^a

Sensitivity ratio of peak with intensity ratio 100 to sensitivity of n-butane at m/e-43.

TABLE I (Continued)

MASS SPECTRA OF CALIBRATION COMPOUNDSTETRAHYDROFURAN, Sensitivity Coefficient = 0.817^a

<u>m/e</u>	<u>(I_{m/e}/I₄₂)</u> <u>x100</u>	<u>m/e</u>	<u>(I_{m/e}/I₄₂)</u> <u>x100</u>	<u>m/e</u>	<u>(I_{m/e}/I₄₂)</u> <u>x100</u>
13	0.2	31	3.5	43	21.5
14	2.1	34	0.2	44	4.2
15	5.1	37	2.2	45	1.0
16	0.2	38	3.9	53	0.3
26	5.4	39	20.6	56	0.2
27	26.1	40	9.5	71	27.8
28	8.5	41	46.1	72	29.9
29	14.5	42	100.0	73	2.5
30	1.6				

DIETHYL ETHER, Sensitivity Coefficient = 0.757^a

<u>m/e</u>	<u>(I_{m/e}/I₃₁)</u> <u>x100</u>	<u>m/e</u>	<u>(I_{m/e}/I₃₁)</u> <u>x100</u>	<u>m/e</u>	<u>(I_{m/e}/I₃₁)</u> <u>x100</u>
14	2.3	31	100.0	46	1.2
15	7.9	41	3.7	59	58.4
26	5.6	42	1.9	60	2.8
27	28.2	43	12.9	73	3.2
28	1.8	44	2.5	74	31.5
29	53.6	45	38.1	75	2.4
30	2.5				

^a Sensitivity ratio of peak with intensity ratio 100 to sensitivity of n-butane at m/e-43.

TABLE I (Continued)

MASS SPECTRA OF CALIBRATION COMPOUNDSn-BUTANOL, Sensitivity Coefficient = 0.594^a

<u>m/e</u>	<u>(I_{m/e}/I₅₆)</u>	<u>m/e</u>	<u>(I_{m/e}/I₅₆)</u>	<u>m/e</u>	<u>(I_{m/e}/I₅₆)</u>
	<u>x100</u>		<u>x100</u>		<u>x100</u>
1	0.3	33	6.1	50	1.2
14	0.9	37	1.3	51	1.3
15	6.2	38	2.5	52	0.5
16	0.3	39	16.4	53	1.2
26	5.5	40	4.0	55	12.7
27	39.7	41	55.0	56	100.0
28	15.4	42	29.2	57	10.0
29	25.2	43	51.6	58	0.7
30	1.6	44	4.4	73	1.6
31	66.0	45	5.9	74	3.7
32	2.5	46	0.6		

2-METHYL FURAN, Sensitivity Coefficient = 0.504^a

<u>m/e</u>	<u>(I_{m/e}/I₈₂)</u>	<u>m/e</u>	<u>(I_{m/e}/I₈₂)</u>	<u>m/e</u>	<u>(I_{m/e}/I₈₂)</u>
	<u>x100</u>		<u>x100</u>		<u>x100</u>
13	0.9	38	10.1	53	62.9
15	6.3	39	48.9	54	21.4
25	1.3	40	4.3	55	4.8
26	9.5	41	4.3	56	1.1
27	34.2	42	4.4	62	0.6
28	23.2	43	10.0	81	55.1
29	11.9	49	5.0	82	100.0
31	0.5	50	17.6	83	10.0
36	0.8	51	18.1	85	0.5
37	7.7	52	8.8		

^a Sensitivity ratio of peak with intensity ratio of 100 to sensitivity of n-butane at m/e - 43.

TABLE 1 (Continued)

MASS SPECTRA OF CALIBRATION COMPOUNDS

FURFURAL, Sensitivity Coefficient = 0.807^a

<u>m/e</u>	<u>(I_{m/e}/I₉₆)</u> <u>x100</u>	<u>m/e</u>	<u>(I_{m/e}/I₉₆)</u> <u>x100</u>	<u>m/e</u>	<u>(I_{m/e}/I₉₆)</u> <u>x100</u>
1	0.1	37	16.4	60	0.2
12	0.7	38	23.1	61	0.2
13	1.2	39	69.0	62	0.2
14	2.0	40	9.4	65	0.3
16	0.2	41	2.7	66	1.5
18	0.8	42	5.3	67	3.1
24	0.5	43	0.6	68	2.1
25	1.9	44	1.0	69	0.8
26	3.5	46	0.1	70	0.3
27	0.9	48	0.8	77	0.2
28	4.2	49	1.9	93	0.3
29	21.3	50	3.4	94	0.7
30	0.4	51	2.5	95	86.9
31	0.1	52	1.0	96	100.0
33	0.2	53	1.9	97	12.7
34	1.0	54	0.2	98	1.0
36	2.4	55	0.1		

^a Sensitivity ratio of peak with intensity ratio 100 to sensitivity of n-butane at m/e-43.

TABLE I (Continued)

MASS SPECTRA OF CALIBRATION COMPOUNDS

FURFURYL ALCOHOL, Sensitivity Coefficient = 0.249^a

m/e	(I _{m/e} /I ₉₈)	m/e	(I _{m/e} /I ₉₈)	m/e	(I _{m/e} /I ₉₈)
	x100		x100		x100
12	0.6	43	16.4	67	2.1
13	1.4	44	11.2	68	3.9
14	5.0	45	2.6	69	32.8
15	6.6	46	0.5	70	40.6
24	0.3	47	0.5	71	7.0
25	2.0	48	0.6	72	0.9
26	10.9	49	5.3	73	0.5
27	34.0	50	16.8	74	1.1
28	19.9	51	22.1	75	0.5
29	41.6	52	16.2	78	1.3
30	4.3	53	51.1	80	1.9
31	18.8	54	6.1	81	56.7
32	2.4	55	16.1	82	6.8
34	0.4	56	2.3	83	0.6
35	1.6	57	2.0	94	2.2
36	2.1	58	0.9	95	8.6
37	15.6	60	1.1	96	4.1
38	27.9	62	0.7	97	56.2
39	76.5	63	0.5	98	100.0
40	11.1	65	0.8	99	16.1
41	75.2	66	3.1	100	1.1
42	64.0				

^a Sensitivity ratio of peak with intensity ratio 100 to sensitivity of n-butane at m/e-43.

TABLE I (Concluded)

MASS SPECTRA OF CALIBRATION COMPOUNDS

CYCLOHEXANE, Sensitivity Coefficient = 0.836^a

<u>m/e</u>	<u>(I_{m/e}/I₈₄)</u>	<u>m/e</u>	<u>(I_{m/e}/I₈₄)</u>	<u>m/e</u>	<u>(I_{m/e}/I₈₄)</u>
	<u>x100</u>		<u>x100</u>		<u>x100</u>
15	3.1	42	27.5	57	5.3
26	4.0	43	15.0	65	1.3
27	23.6	50	2.1	67	3.6
28	20.2	51	2.8	68	2.0
29	9.3	52	2.0	69	26.0
38	2.9	53	2.4	70	1.9
39	29.8	54	6.6	83	6.7
40	6.1	55	32.3	84	100.0
41	55.2	56	94.3	85	7.4

METHYL CYCLOHEXANE, Sensitivity Coefficient = 0.758^a

<u>m/e</u>	<u>(I_{m/e}/I₈₃)</u>	<u>m/e</u>	<u>(I_{m/e}/I₈₃)</u>	<u>m/e</u>	<u>(I_{m/e}/I₈₃)</u>
	<u>x100</u>		<u>x100</u>		<u>x100</u>
15	3.5	51	2.8	70	35.8
27	28.4	52	1.1	71	1.0
28	13.4	53	6.8	81	1.8
29	13.8	54	5.0	82	17.0
38	2.3	55	75.2	83	100.0
39	28.9	56	31.0	84	7.6
40	5.0	57	5.5	97	2.6
41	51.6	63	1.7	98	72.3
42	32.6	67	5.2	99	7.7
43	8.0	68	9.3	100	2.6
50	2.1	69	20.5		

^a Sensitivity ratio of peak with intensity ratio 100 to sensitivity of n-butane at m/e-43.

TABLE II
PUMPING COEFFICIENTS FOR VARIOUS MOLECULES

<u>Compound</u>	<u>Molecular Weight</u>	<u>(M.W.)^{-1/2}</u>	<u>$\beta \times 10^3$, sec.⁻¹</u>
Hydrogen	2	0.707	15.44
Methane	16	0.250	5.618
Ammonia	17	0.243	3.233
Water	18	0.236	3.562
Acetylene	26	0.196	3.972
Ethylene	28	0.189	4.760
Nitrogen	28	0.189	4.143
Carbon Monoxide	28	0.189	4.230
Oxygen	32	0.176	4.178
Methanol	32	0.176	3.245
Hydrogen Sulfide	34	0.171	3.956
Propylene	42	0.154	3.042
Carbon Dioxide	44	0.151	3.067
Propane	44	0.151	3.135
Acrylonitrile	53	0.137	2.588
n-Butane	58	0.131	2.649
Acetone	58	0.131	2.556
Isopropanol	60	0.129	2.369
Acetic Acid	60	0.129	1.602
Tetrahydrofuran	72	0.118	2.374
Diethyl Ether	74	0.116	2.339
n-Butanol	74	0.116	1.909
Benzene	78	0.113	1.530
2-Methyl Furan	82	0.110	2.068
Toluene	92	0.104	1.685
Phenol	94	0.103	1.710
Furfural	96	0.102	1.640
Furfuryl Alcohol	98	0.101	1.216
Cyclohexane	98	0.101	2.110
Benzonitrile	103	0.0985	1.138
o-Xylene	106	0.0971	1.591
Methyl Cyclohexane	112	0.0945	1.877
Hexachloroethane	234	0.0645	0.705

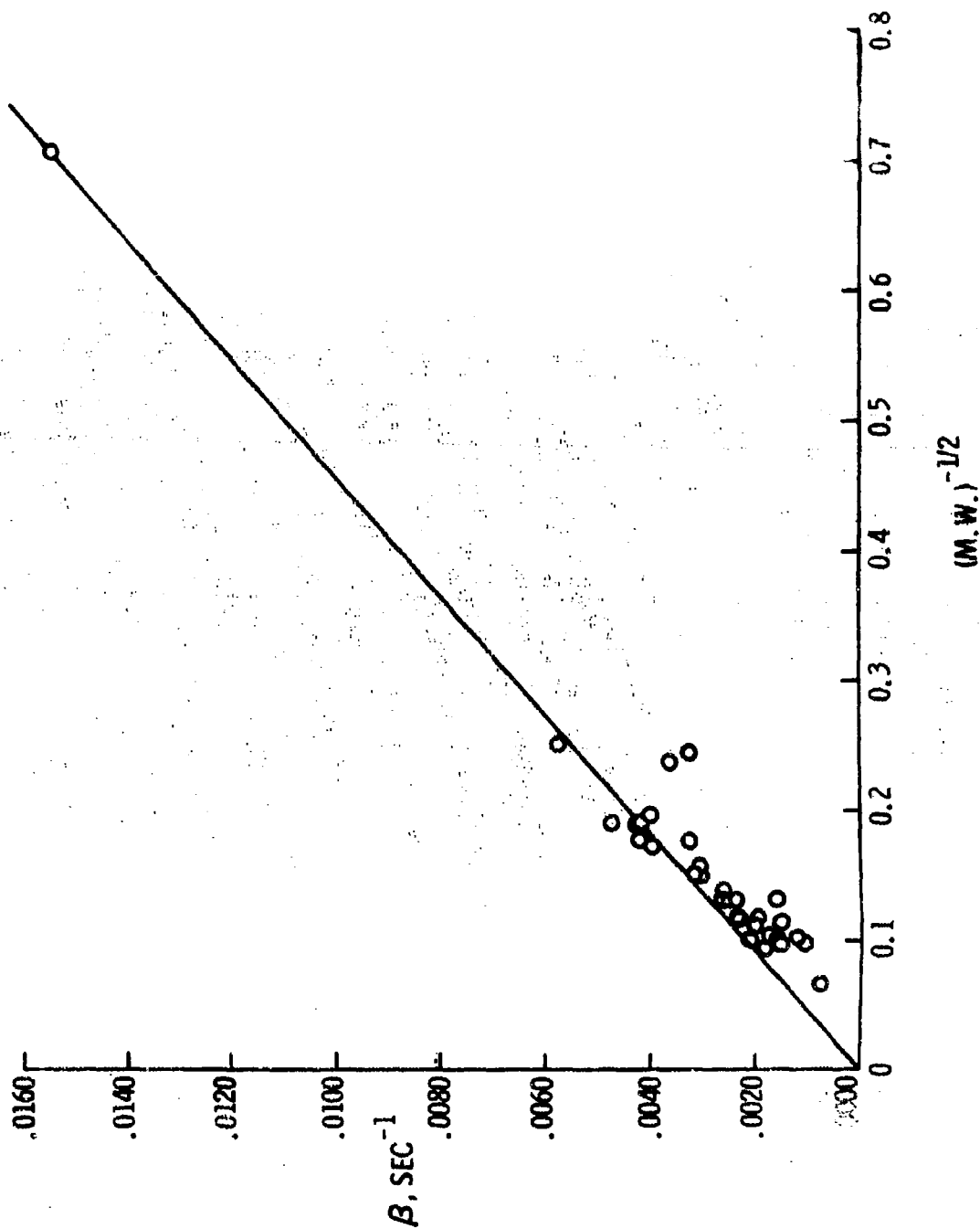


Figure 3. Pumping Coefficients for Various Molecules

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SECTION V

MTA OF POLYMERS

Four polymer samples have been successfully subjected to MTA during the period of this report, as listed in Table III. The weighing errors associated with % weight loss are large, as explained in reference 5.

A. Bis Benzimidazo Benzophenathroline Ladder Polymers

The ordinary and end-capped BBL polymers were prepared as described by Arnold and Van Deusen (Ref. 14). Residue weights as reported in Table III are thought to be accurate for the film samples produced film char residues, and these were weighed separately. Selected mass spectra are shown in Figures 4 and 5 for the ordinary and end-capped polymers, respectively. Overloading occurred for the ordinary polymer at m/e-28 (CO) from about 730-760°C. Otherwise, the data were of extremely high quality. On the whole, data for the end-capped polymer were excellent, but there was a loss of signal that influenced several mass peaks at about 690°C. The instrument returned to normal after that event, but the mass spectrometer filament failed soon after the run was completed. Overloading also occurred at m/e-28 in this run, between 730 and 780°C.

Spurious mass peaks appeared at the usual positions, e.g. m/e-55 and 70 (see ref. 5), so a blank pyrolysis was carried out on 27 March 1969. Data processing was performed and the results were compared with an earlier blank experiment (28 March 1967). The new blank was found to be quite similar to the old one, and it appeared to account for all of the spurious peaks and indicated minor products, such as benzene and benzonitrile. Several other blank experiments were carried out with careful cleaning and flaming of the water cooled jacket region, since some deposits were observed there. Cleaning, however, did not eliminate the blank spectra, but complete data processing was not carried out for the later blank runs. The blank spectra were taken into account for quantitative analysis.

Quantitative analyses were performed for the two BBL polymer MTA experiments. The following equation was used

$$n = -\phi V K_t / R \gamma T$$

where n = moles, ϕ = calibration pumping coefficient, sec^{-1} ($2.303 \times$ value of β in Table II), V = calibration volume ($7,698 \text{ cm}^3$), K_t = area under curve of ion intensity vs. time ($6 \times K_T$, where K_T = area vs. temperature), R (gas constant) = $82.06 \text{ cm}^3 \text{ atm} / ^\circ\text{K mole}$, γ = sensitivity, moles/atm ($2.66 \times 10^7 \times S$, where S = value of sensitivity coefficient in Table I and ref. 5), $T = 300^\circ\text{K}$. In practical units

TABLE III
SUCCESSFUL MTA EXPERIMENTS

<u>Polymer</u>	<u>Code</u>	<u>Date</u>	<u>Sample Wt.</u> <u>mg.</u>	<u>Wt. Loss</u> <u>%</u>
bis benzimidazo benzophenathroline ladder polymer (end-capped)	BBL-SN2-EC	3/14/69	1.492	32.5
bis benzimidazo benzophenathroline ladder polymer	BBL-SN2	3/18/69	1.130	36.4
bis benzimidazo benzophenathroline polymer	BBB	8/12/69 ^a	1.136	22.6 ^c
bis benzimidazo benzophenathroline polymer	BBB	8/29/69 ^b	1.037	21.3 ^d

^a Only m/e-28 scanned

^b Scanned from m/e-0 to 52

^c Heated to ~890°C

^d Heated to ~920°C

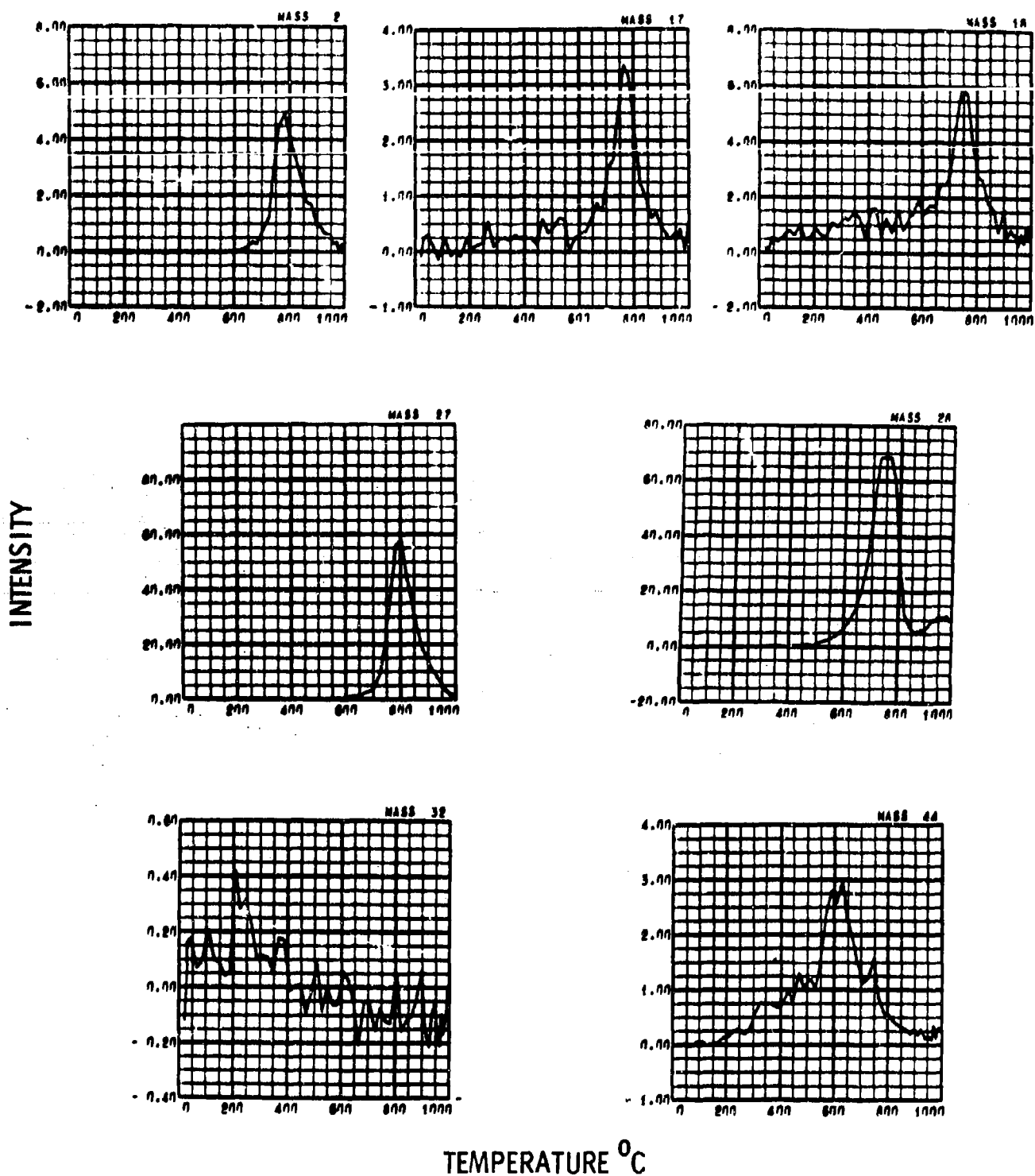


Figure 4. Representative Standardized MTA Results for Bis
Benzimidazo Benzophenanthroline Ladder Polymer
(BBL-SN2)

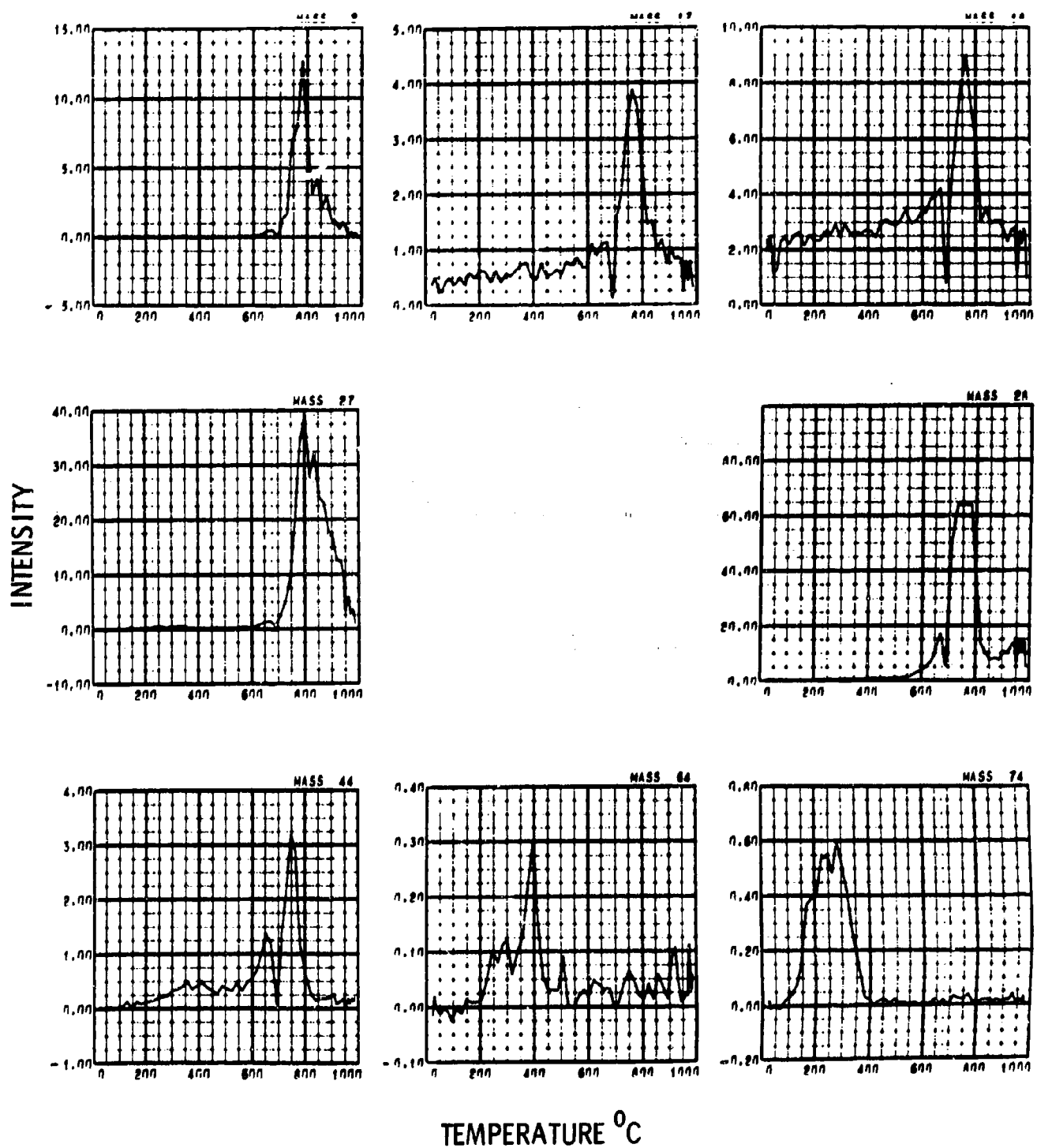


Figure 5. Representative Standardized MTA Results for End-Capped Bis Benzimidazo Benzophenathroline Ladder Polymer (BBL-SN2-EC)

$$n = -1.624 \times 10^{-7} \beta K_T / S$$

Errors could creep in at the lowest and highest temperatures, because of departures from linearity. This source introduces a negative error when gases were evolved during those periods. The assumed value of temperature was a further source of error. While the bulk of the zone from which the sample enters is at ambient temperature, there are some departures. The furnace tube varies from room temperature to 1000°C. A water cooled jacket is between the furnace tube and the mass spectrometer. The portion of mass spectrometer where the molecules first enter the instrument is at an elevated temperature. Therefore, the 300°K value is probably too low and elevates the resulting calculation. The results for polymer BBL SN2 and BBL SN2 EC are listed in Tables IV and V, respectively. Sensitivity values for hydrogen cyanide and sulfur dioxide were taken from the literature (ref. 15), and β values were estimated from Figure 3. Except for methanol (BBL SN2), diethyl ether (BBL SN2 EC) and sulfur dioxide (BBL SN2 EC), the products were pretty much the same and evolved over pretty much the same temperature range. Carbon monoxide was the main product, followed by hydrogen cyanide and hydrogen. Carbon monoxide was the first product. Hydrogen cyanide, water (the main part), ammonia and hydrogen were evolved pretty much concurrently. Nitrogen evolution could not be estimated with any significant degree of accuracy, for it was swamped by carbon monoxide. There was, however, a small reduction of carbon dioxide, hydrogen cyanide, water and hydrogen for the end capped polymer (BBL SN2 EC), ranging between 25 and 45%.

Note that in each case the calculated weight loss was almost exactly 62% higher than the observed value, indicating great consistency in the computations.

B. Bis Benzimidazo Benzophenathroline Polymers

Two special MTA runs were carried out for Celanese BBB polymer. In the first experiment, the gate was fixed at m/e-28, since CO has been shown to be the major product evolved from this type of polymer (refs. 4, 5). Data points were recorded on perforated paper tape, but were read every 15 sec., or approximately every 2.5°C, thus allowing many data points to be recorded for the purpose of kinetic analysis. In the usual 200 point scans, data points are recorded every 18-20°C. Temperatures were corrected for slidewire errors and for the fact that temperatures and ion intensities were recorded at slightly different times. Intensities were corrected for background. A graph of the results is shown in Figure 6. Gas evolution started at about 450°C and peaked at about 720°C. Carbon monoxide was used as the calibration standard instead of n-butane. It was found that one volt was equivalent to 2.188×10^{-10} moles/sec. entering the mass spectrometer leak.

Since no significant pyrolysis products heavier than carbon dioxide have been observed from BBB polymers* (refs. 4, 5), a run was performed scanning only 40 positions

* It is now thought that spectra attributed to acrylonitrile in earlier work, were contributed by the system.

TABLE IV

MTA RESULTS FROM BIS BENZIMIDAZO BENZOPHENATHROLINE LADDER POLYMER (BBL-SN2)

Product	Evolution Temperature, °C			Yield ^a		
	Start	Peak	Finish	Moles x 10 ⁵	Mole %	Wt. mg.
Carbon Dioxide	150	630	900	0.039	1.4	.0173
Methanol	70	250	500	0.011	0.4	.0035
Carbon Monoxide	400	740	860+	1.270	47.2	.3557
Nitrogen	< 860	~970	1000+	0.071	2.6	.0199
Hydrogen Cyanide	600	800	1000+	0.498	18.5	.1346
Water	50	750	1000	0.162	6.0	.0292
Ammonia	~560	770	920	0.041	1.5	.0070
Hydrogen	600	780	1000	0.599	22.3	.0121
Total				2.691	99.9	.5793 ^b

^a Based on 1 mg. sample^b Actual wt. loss - 0.364 mg.

TABLE V

MTA RESULTS FROM END-CAPPED BIS BENZIMIDAZO BENZOPHENATHROLINE
LADDER POLYMER (BBI-SN2-EC)

Product	Evolution Temperature, °C			Yield ^a		
	Start	Peak	Finish	Moles x 10 ⁵	Mole %	Wt. mg.
Diethyl ether	60	260	450	0.014	0.6	.0103
Sulfur dioxide	130	400	550	0.003	0.1	.0017
Carbon dioxide	100	750	990+	0.025	1.1	.0108
Carbon monoxide	400	760	850+	1.217	55.3	.3409
Nitrogen	<850	~960	990+	0.102	4.6	.0286
Hydrogen cyanide	600	800	990+	0.374	17.0	.1012
Water	40	760	990	0.106	4.8	.0190
Ammonia	~500	760	990	0.039	1.8	.0066
Hydrogen	600	780	990	0.322	14.6	.0065
Total				2.202	99.9	.5256 ^b

^a Based on 1 mg. sample

^b Actual wt. loss- 0.325 mg.

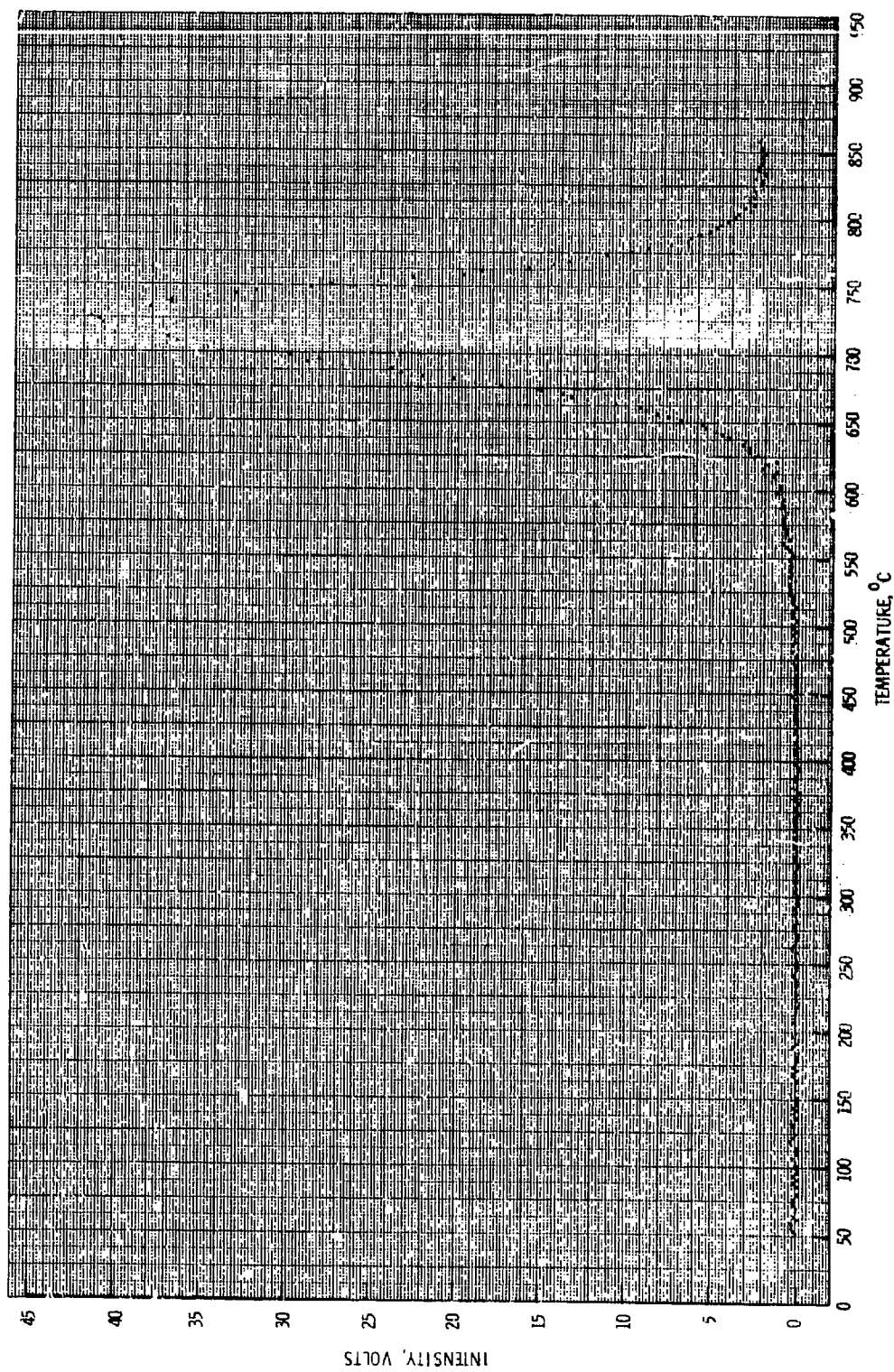


Figure 6. MTA Plot at $m/e-28$ for Single Peak Run on Celanese Bis Benzimidazo Benzophenathroline Polymer

(m/e-0, 1, 2, 12-18, 22, and 24-52) instead of the usual 200 positions. In this case, each mass peak was scanned 5 times more frequently than before, thus allowing better time resolution. Point-to-point temperature separation was found to be about 3.85°C for each mass. The perforated paper tape was converted to a digital magnetic tape using the new program described in section III. Background and run data for m/e-0 and 28 were analyzed manually, and yielded the results shown in Figure 7. In this case, CO evolution started at about 450°C , once again, but peaked at 705°C . Data for CO_2 (m/e-44) and HCN (m/e-27) were also examined visually. The CO_2 evolution was similar to those for the BBL polymers, in contrast to the copious CO_2 evolution from the earlier BBB experiments. In addition, more HCN was evolved than in the earlier experiments, but less than for the BBL polymers. Relative H_2O evolution was just the reverse of HCN.

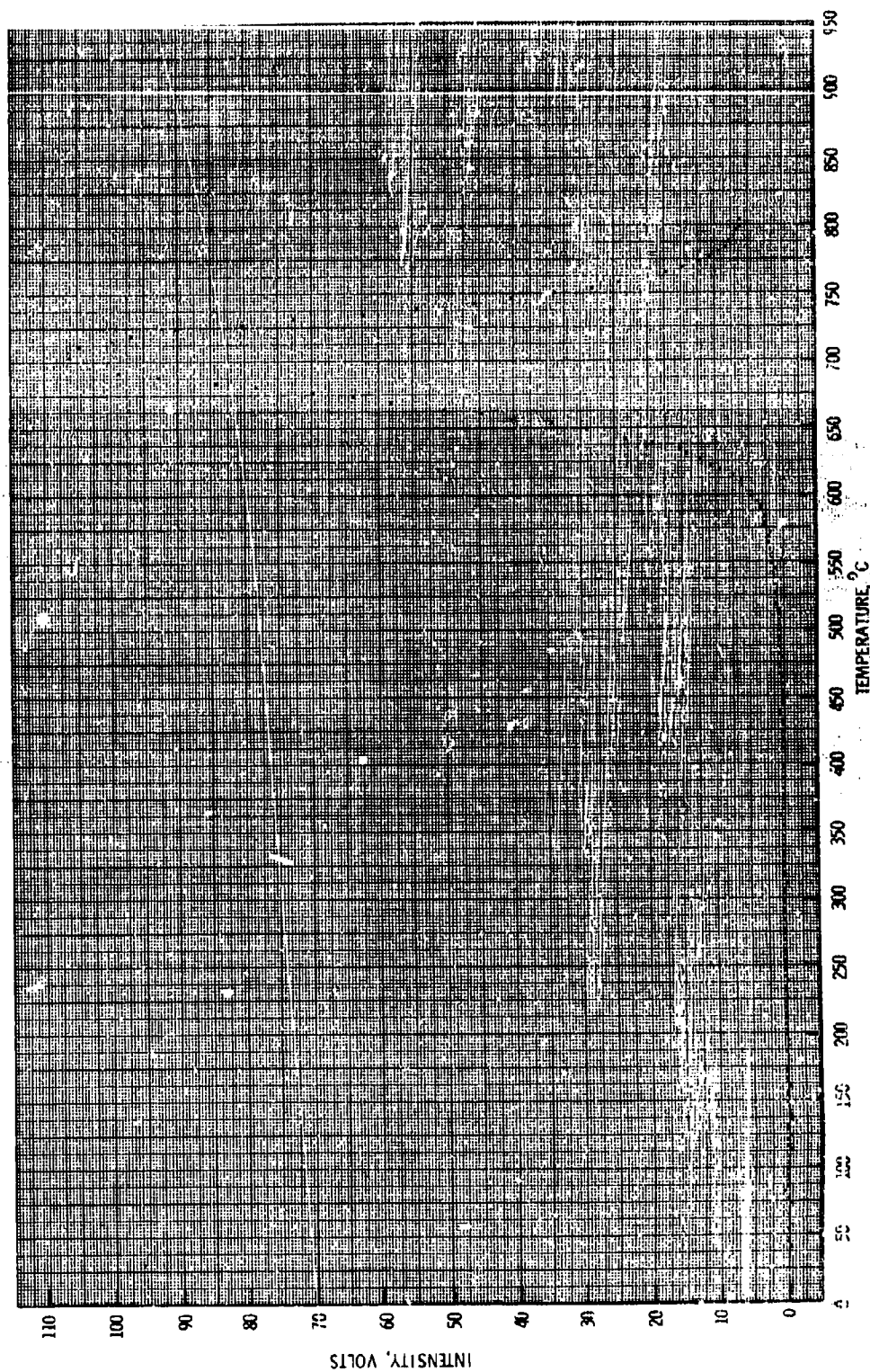


Figure 7. MTA Plot at m/e-28 for 40 Peaks/Scan Run on Celanese Bis Benzimidazo Benzophenathroline Polymer

SECTION VI

DISCUSSION

A. Bis Benzimidazo Benzophenathroline Polymers and Ladder Polymers

The thermal stability of BBL polymers does not appear to be greatly influenced by whether or not the polymer is end-capped, as shown by the temperature of onset of decomposition gas evolution. There was, however, a small increase in char yield for the end-capped polymer. Arnold and Van Deusen (ref. 14) reported the results of thermogravimetric (TG) decomposition of these polymers at 3°C/min. in nitrogen atmospheres. The end-capped polymer was slightly less volatilized (18% vs. 22%) at 900°C. These are in the same order as for MTA (Table III). The MTA samples were more volatile than the TG samples, but the former were heated 100°C hotter. Other experimental differences, such as sample size, container geometry, heating rate, and atmosphere, could influence residue weight. The end-capped polymer was slightly more stable in the TG test, as shown by the temperature of onset of weight loss.

Before comparing the results for BBL and BBB polymers, it is necessary to compare the latest BBB results with the earlier ones. In studying the oxidation of BBB polymers, Conley and Caudiana (ref. 16) observed only CO, CO₂, H₂O and traces of (CN)₂. Since the most recent BBB experiment showed a vast reduction of CO₂, together with decreased H₂O and increased HCN, it may be assumed that the earlier BBB sample (m-BB-2) had been oxidized, perhaps during synthesis. Although data processing has not been completed, it seems that more HCN forms in the pyrolysis of the BBL polymers, and this may be related to differences in rigidity of the molecules. It would be interesting to compare elemental analysis of the residues from the two polymers, especially for nitrogen content.

The following discussion is concerned with the m/e-28 peaks obtained for the three BBB polymers. The values in Figure 21 of reference 5 (m-BB-2) were recalculated to include a more accurate temperature correction, and were replotted in Figure 8. In comparing the two plots for m-BB-2, it is apparent that the present plot provides far more intensity resolution than the automatic graph plotter. This is not surprising for resolution in the y-axis is about 1 part in 1,000 over the entire sheet, or about 1 part in 300 on each graph for a nine graph sheet. Since the total y-axis scale for m/e-28 (Figure 21, ref. 5) is 200 units, the resolution is only 2/3 volts. This is not adequate to detect the onset of evolution for a strong peak. Figure 8 shows that the onset of evolution was at about 450°C for the earlier run, in agreement with the present runs (Figures 6 and 7). A more accurate judgement may be made for 2.5°C separation (Figure 6), than for 3.85°C separation (Figure 7). The 18.0°C average separation in Figure 8, renders this curve the least satisfactory for that purpose. Each of the m/e-28 peaks contains a contribution from CO⁺ due to fragmentation of CO₂. The levels are small, in Figures 6 and 7,

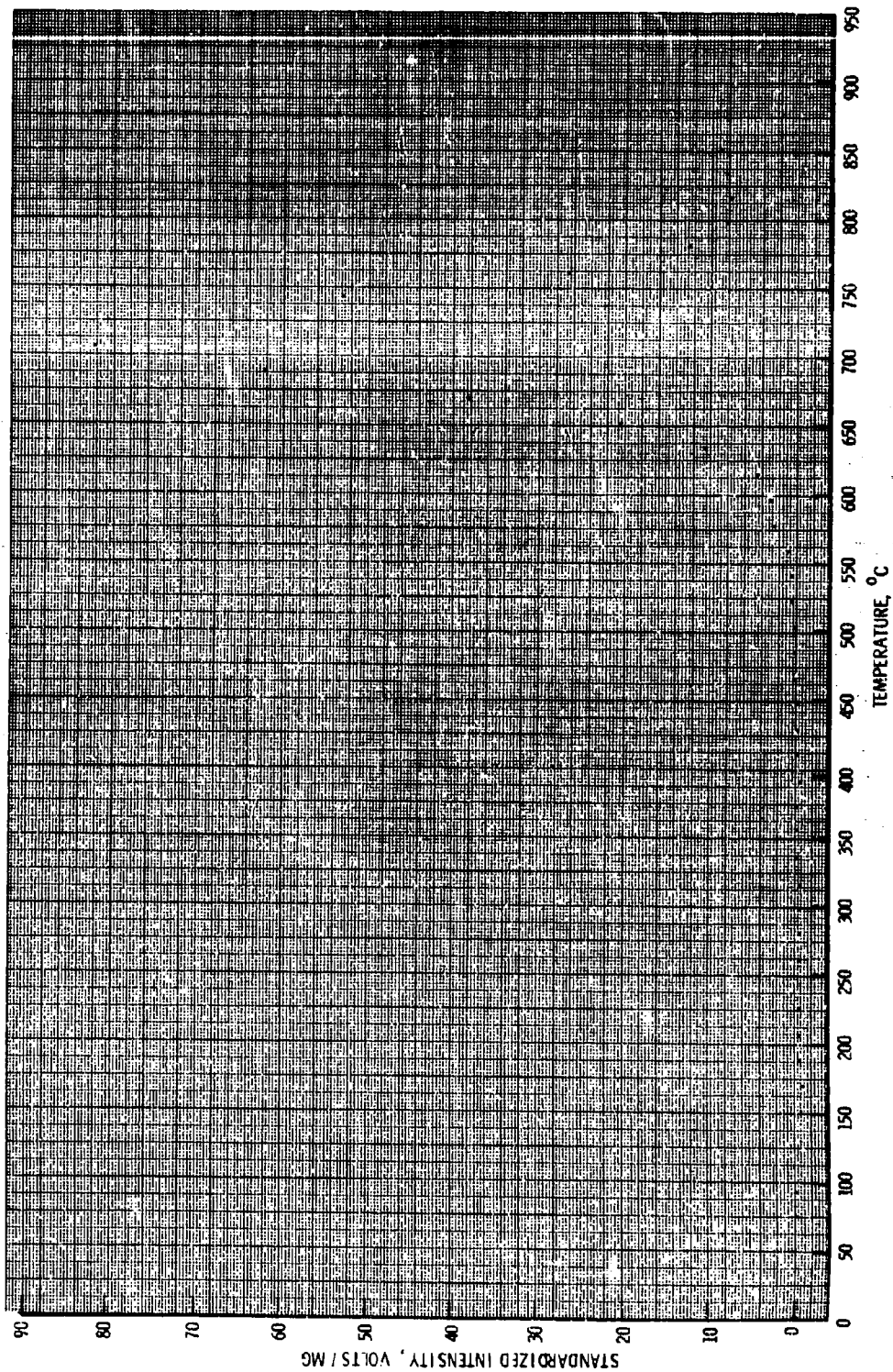


Figure 8. Standardized MTA Plot at m/e-28 for Earlier Bis Benzimidazo
Benzaphenathroline Polymer (m-BB-2)

because the 28/14 ratio for CO_2 is 0.992, and the CO_2 yield for the Celanese BBB polymer is relatively small. The CO_2 contribution in Figure 8 is somewhat more significant, but would not particularly influence its shape. The three curves are slightly displaced from each other, although they have the same general shapes. The evolution in Figure 7 appears to be at the lowest temperature, and Figure 6 shows the highest. The peak temperatures are approximately 705°C (Figure 7), 715°C (Figure 8) and 720°C (Figure 6). Several experimental variables, including particle size and sample distribution are known to influence peak temperature and shape of gas evolution curves. It is obvious that because of experimental scatter, the quality of the MTA curve is better for a greater number of points.

B. Aliphatic Polyesters

The results of MTA of aliphatic polyesters (refs. 4, 5) were reviewed. The formation of succinic anhydride from poly(octamethylene succinate) (O-1) suggested that cyclic anhydrides form from thermal decomposition of the diacid part of the molecule. Cyclohexanone, cyclopentanone, and cyclobutanone are reasonable products from decarboxylation of pimelic, adipic, and glutaric anhydrides, respectively, from poly(octamethylene pimelate) (O-4), poly(octamethylene adipate) (O-3), and poly(octamethylene glutarate) (O-2). The sebacate polyesters may perhaps yield sebacic anhydride, but that molecule may decompose to smaller fragments than cycloheptanone.

SECTION VII

CONCLUSIONS

A number of conclusions about the various polymers subjected to MTA in this and earlier studies are included in Sections V and VI and will not be repeated here.

The MTA system is functioning well as shown by the good quality of data. The mass spectrometer continues to produce calibration spectra that are reasonable as shown by comparison with the literature.

The correlation of pumping rates with molecular weight are reasonable, but there are obvious departures that are important. It would be beneficial to account for these in order to obtain the most accurate kinetic parameters.

It is clear that frequent scanning improves the quality of the data in various ways. Because of the scatter inherent in the system, only with frequent scanning is it possible to obtain an accurate MTA curve shape. Thus, frequent scanning permits greater accuracy in determining the temperature of the onset of the evolution of each product, peak temperature, and evaluation of kinetic parameters.

The following papers were presented during the period of this research:

"Kinetics by DTA-A Critique," by H. L. Friedman, presented at the Third Toronto Symposium on Thermal Analysis, Toronto, Ontario, February 25-26, 1969; to be published in the Proceedings of the Symposium.

"The Application of Mass Spectrometric Thermal Analysis to Pyrolysis of Aliphatic Polyesters," by H. L. Friedman, presented at the Symposium on Thermal Analysis-Mass Spectrometry, at the 17th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, May 18-23, 1969.

SECTION VII

RECOMMENDATIONS FOR FUTURE WORK

Complete revision of the data sorting and plotting programs for the G. E. 635 Computer.

Build potentiometer for random selection of up to 20 mass peaks.

Complete data analysis of 40 peak scan run for MTA of Celanese bis benzimidazo benzophenathroline polymer.

Carry out limited peak run and data processing for bis benzimidazo benzo-phenathroline ladder polymer.

Run MTA pyrolysis of new polymer samples as they are received.

Continue to carry out calibration runs and data processing for samples of products expected from preliminary analysis of completed runs.

Carry out approximate quantitative analysis, based on most reasonable comparison of MTA traces and calibration data.

Carry out kinetic analysis for selected products, and relate to decomposition mechanisms when possible.

Examine resulting information and compare with existing knowledge to determine quantitative relationships on the overall influence of chemical structure on thermal stability which will cover wide varieties of new high temperature polymers.

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11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Nonmetallic Materials Division Air Force Materials Laboratory Wright-Patterson Air Force Base, Ohio	
13. ABSTRACT Research was continued using mass spectrometric thermal analysis (MTA) to study the thermal degradation of various polymers. Several samples of bis benzimidazo benzophenathroline (BBB) polymer and its ladder (BBL) polymers were successfully subjected to MTA. Quantitative results were obtained for ordinary and end-capped BBL polymers, and the effects of end-capping were discussed. BBB runs were carried out in modified fashions that allowed greater frequency of scanning of a limited mass range. The effects of varying the frequency were discussed. The results for BBL polymers and for the present and earlier BBB polymers were compared. A discussion on some aspects of the mechanism of thermal degradation of aliphatic polyesters was included, as the result of reviewing earlier data. Calibration results were reported for seventeen compounds. Pumping coefficients for thirty three compounds were compared. Tests were carried out for new furnace systems in a more modern time-of-flight mass spectrometer, which was equipped with a differentially pumped region near the electron beam. Computer programs are in the process of being rewritten for a new computer and to permit greater flexibility in experimental technique and in data processing.			

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